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Phosphate Esters

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I. INTRODUCTION

Since the discovery of their lubricating and antiwear properties prior to World War II, phosphate esters have been significant factors in the lubricants industry. Through years of research and practical experience, industry has learned to manufacture and formulate these versatile chemicals to satisfy a wide variety of demanding application conditions. The phosphate esters that have survived today as commercially important products have proven to be outstandingly useful, stable, and safe additives, fluids, and lubricants.

Phosphate esters are the most fire resistant of the reasonably priced synthetic base stocks. Their high fire point, flash points, and autoignition temperatures, and extraordinarily low vapor pressures make them very difficult to ignite. Their low heats of combustion make them self-extinguishing fluids. Over 50 years of use has shown them to be excellent lubricating agents with exceptional thermal, hydrolytic, and oxidative stability in difficult operating environments. Shortcomings identified in the early years of development (hydrolytic stability, viscosity index, neurotoxicity) have been conquered by optimizing manufacturing techniques, raw materials, and stabilizer systems.

This chapter describes the chemistry and production of this class of phosphorus compounds, esters of phosphoric acid, outlining the physical and chemical properties that make them practical, useful, and important industrial chemicals. We review the formulation of the phosphate esters into lubricants and hydraulic fluids, with emphasis on commercial applications. Finally, we outline practical methods of managing systems employing phosphate esters to achieve optimum working life and cost-effective performance in the industrial environment.

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A. Historical Development

Although thousands of organophosphorus compounds have been synthesized, only those classified as phosphate esters, or fully substituted esters of orthophosphoric acid (H_3PO_4), have become commercially significant in the synthetic lubricants field. While mono-, di-, and trisubstituted esters have found commercial use in a variety of areas including lubricant additives, only the neutral tertiary esters are used as synthetic lubricants or fluids.

Tertiary orthophosphate esters have been known for over 140 years, the trialkyls having been synthesized in about 1849 [1] and the triaryls in about 1854 [2]. The development, after World War I, of less flammable nitrocellulose lacquers plasticized with tricresyl phosphate (TCP) as industrial and automotive coatings [3], led to the investigation of phosphate esters for safer hydraulic fluids and lubricants. During the 1930s a number of investigators [4–7] defined the lubricating properties of phosphate esters, especially their usefulness as antiwear agents.

During World War II and the years immediately following, the development of increasingly sophisticated military and commercial aircraft, which used hydraulic rather than mechanical control systems, created a need for safe, nonflammable, hydraulic fluids. J. D. Morgan, working at the Cities Service Oil Company, was awarded patents in 1944 and 1946 [8,9] on lubricant and hydraulic fluid compositions having wide operating temperature ranges (−40 to 200°F) based on tributyl and other trialkyl phosphates. Also in 1946, W. F. Hamilton and coworkers at the Lockheed Aircraft Corporation [10] were awarded a patent on what can be considered the forerunner of today's commercial aircraft hydraulic fluids.

The use of both trialkyl and triaryl phosphates as synthetic base stocks was more thoroughly defined and developed in a major program jointly sponsored by the U.S. Navy and Air Force at the Shell Development Company between 1949 and 1953 [11]. F. J. Watson was awarded several patents for fluid compositions based on tributyl and tricresyl phosphates [12–14].

At about the same time, the Douglas Aircraft Company and Monsanto Chemical Company helped pioneer the use of phosphate esters in commercial jet aircraft [15–18]. By the late 1950s, such planes as the Douglas DC-8, Boeing 707, and Convair 880 were flying on Monsanto's Skydrol® 500A fluid, which was based on a mixed alkyl aryl phosphate.

Concurrent with the use in aircraft, other commercial uses developed. Tricresyl phosphate and other esters became widely used during the 1950s as deposit modifiers in leaded gasoline. By the late 1950s Monsanto, Celanese Corporation of America, and the E. F. Houghton Company had complete lines of phosphate ester based industrial hydraulic fluids, which were readily adopted by the steel, aluminum, foundry, and casting industries. Each company also marketed phosphate ester products for use as fire-resistant compressor lubricants. The U.S. Navy, in 1961, adopted specification MIL-H-19457, a fire-resistant fluid then based on trixylenyl phosphate, for use in aircraft carrier elevators.

Some of the early industrial fluids developed both in the United States and Europe were based on alkyl aryl phosphates and contained chlorinated aromatic hydrocarbons (chlorinated biphenyls); environmental problems that surfaced subsequently resulted in the complete disappearance of these fluids from commercial use. The industrial phosphate ester fluids used today are all based on triaryl phosphates containing no halogenated components either as additives or base stocks.

II. CHEMISTRY

A. Structure

Numerous organic phosphorus compounds including phosphites, phosphonates, and phosphates have found application as additives in a variety of lubricant formulations as stabilizers, antiwear

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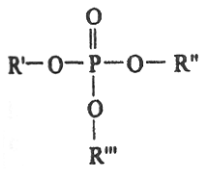
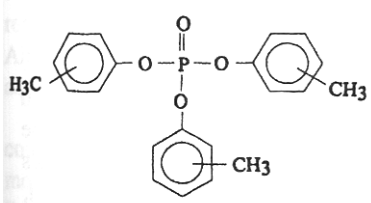
additives, antioxidants, metal passivators, and extreme pressure additives. Of these, the zinc dialkyl dithiophosphates, found in virtually all automotive engine lubricants, are the most widely used and best known. Only one group of phosphates, the trisubstituted (tertiary), neutral esters of orthophosphoric acid, has found significant use as synthetic base stocks. These compounds have the general structure:

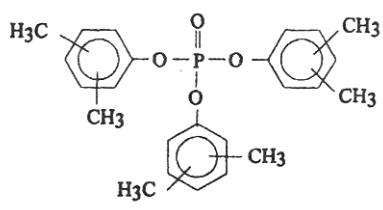


None of the commercially important base stocks contain nitrogen, sulfur, chlorine, or other elements substituted in the R groups. Although metallic or amide derivatives of the partial esters have found use as lubricant additives, all the significant commercial synthetic lubricant base stocks are compounds in which all three R groups are alkyl or aryl moieties containing four or more carbon atoms, hydrogen, and oxygen. Thus, the important phosphate ester base stocks fall into three broad classes: triaryl, trialkyl, and aryl alkyl phosphates, and the remainder of this chapter emphasizes these compounds.

The triaryl phosphates are the most significant commercial products. The first significant compounds, tricresyl phosphate (TCP) and trixylenyl phosphate (TXP), were often referred to as "natural" esters because the cresol and xylenol raw materials come from petroleum or coal tar refining. In this group of compounds all three organic groups are usually the same:



Tricresyl phosphate



Trixylenyl phosphate

Commercial production of TCP and TXP usually starts with a mixed meta/para isomer feedstock. The ortho content, for toxicological reasons, is often specified below 1% by weight. Cresol, xylenol, and phenol can be blended and used to produce mixed esters; cresyl diphenyl phosphate (CDP) is the most significant of these.

During the 1960s, "synthetic" analogues of the natural esters were developed which reduced both toxicological concerns and production costs. Isopropylphenyl and tertiary butylphenyl phosphates are now commercially available in a variety of viscosity grades. Because these products are always made from a mixed feedstock of phenol and the respective alkyl phenol, they are more properly referred to as triphenyl phosphate, propylated or isopropylphenyl phenyl phosphate (IPPP), and triphenyl phosphate, butylated or *tert*-butylphenyl phenyl phosphate (TBPP). The structure of diphenyl-para-*t*-butylphenyl phosphate, the dominant species in a widely used ISO 46 base stock, is as follows:

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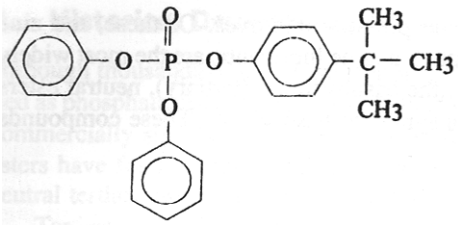

Diphenyl, para-*t*-butylphenyl phosphate

All commercial synthetic triaryl phosphate fluid base stocks are mixtures of varying molecular weights. The location of substituents on the phenyl ring can vary among the ortho, meta, and para positions. In the lower viscosity synthetic products, unsubstituted triphenyl phosphate (TPP) is usually the most significant component species. Increasing the proportion of alkyl phenol in the production feedstock increases average molecular weight, viscosity, specific gravity, and complexity of the mixture and lowers phosphorus content of the final product.

Commercially available trialkyl phosphates are typically symmetrical ($R' = R'' = R'''$). Tri-*n*-butyl phosphate (TBP), used in aircraft hydraulic fluid, is the most important of the synthetic base stocks today, but there has been recent interest in triisobutyl phosphate (TiBP), tributoxy-ethyl phosphate (TBEP), and trioctyl phosphate (TOP) for new base stock development.

Dibutylphenyl phosphate (DBPP), also used in aircraft fluids, is the most common alkyl aryl ester. Although a significant patent estate developed on alkyl aryl esters, and several of them were used widely at one time as industrial fluid base stocks, there is little significant commercial use of these esters today other than the dibutylphenyl and the isodecyldiphenyl esters. Most alkyl aryl esters find use as flame-retardant plasticizers in the thermoplastics industry.

B. Production

Although the tertiary phosphates are described as esters of orthophosphoric acid, preparation from the acid gives poor yields because the water produced readily hydrolyzes the ester in the acidic conditions of the reaction. Because of the differences in the reactivity of starting materials and the chemistry of the products, distinct commercial routes have developed to produce triaryl, trialkyl, and alkyl aryl esters.

1. Triaryl Phosphates

The simplest laboratory preparation of triaryl esters and the most important commercial route, is the phosphorylation of an aromatic alcohol—that is, a phenolic compound—with phosphorus oxychloride in the presence of magnesium or aluminum chloride [19]:

$$3ROH + POCl_3 \xrightarrow{100\text{–}200^\circ C} (RO)_3P{=}O + 3HCl \qquad (1)$$

An excess of the phenolic compound is maintained to avoid the presence of the intermediate chloridates, $(RO)(Cl)_2P{=}O$ and $(RO)_2(Cl)P{=}O$, which would reduce yields and produce acidic partial esters during subsequent processing.

Prior to the early 1960s, cresylic acids were the raw materials used for this preparation. The common cresylic acids (cresol, xylenol, and mesitol) have one, two, and three methyl groups on the ring, respectively, in any of the ortho, meta, and para positions. Trixylenyl phosphate became the most commonly used industrial fluid base stock of the triaryl esters. The range of

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viscosities required for industrial uses could be achieved by carefully selecting the xylenol isomers used as the starting material. An isomer mixture consisting of mostly 3,5-xylenol gives a higher viscosity than the 2,6-mixture, for example.

Work by the Albright & Wilson Company [20] and the Ciba-Geigy Corporation [21] in the United Kingdom in the 1960s resulted in the development of a more easily controlled and less expensive route to the range of products desired. Work at both companies involved the catalytic alkylation of phenol with propylene or butylene and the subsequent reaction of this "synthetic alkylate" with phosphorus oxychloride.

In the synthetic process, the viscosity of the final product can be controlled in either or both of two ways: by the degree of alkylation of the phenol (i.e., by the number of alkyl groups on the phenol ring) and by using a variable, mixed feed of phenol and alkyl phenol to the phosphorylation reaction [22]. As the degree of alkylation increases, or the proportion of unalkylated phenol decreases, the viscosity of the product increases. Thermodynamics and steric hindrance determine which alcohols react faster (phenol is fastest) and thus determine the molecular weight and isomer distribution in the final product. The commercial process is therefore more appropriately described as follows:

$$x\mathrm{ROH} + (3 - x)\,\mathrm{R'OH} + \mathrm{POCl_3} \rightarrow (\mathrm{RO})_3\mathrm{P{=}O} + (\mathrm{RO})_2(\mathrm{R'O})\mathrm{P{=}O} + (\mathrm{RO})(\mathrm{R'O})_2\mathrm{P{=}O} + (\mathrm{R'O})_3\mathrm{P{=}O} + 3\mathrm{HCl} \quad (2)$$

For both the natural and synthetic esters, a variety of refining steps are used to produce the final product. By-product hydrogen chloride (HCl) can be removed from the reaction by heating, partial vacuum, sweeping with an inert gas, or reaction with an organic base such as pyridine. The most common method combines heating and vacuum followed by scrubbing through water to recover the HCl as by-product hydrochloric acid solution.

Following the HCl extraction, the crude product is refined. In one method, a series of distillation steps first removes the unreacted phenols and alkyl phenols for recycle, and isolates the refined product, leaving the catalyst and high-boiling by-products in the still residue [23,24]. Alternately, the crude product can be distilled to remove unreacted raw materials, washed with aqueous alkali and water, and dried under vacuum [19].

The foregoing discussion of the production chemistry and raw materials indicates that most commercial triaryl esters are not symmetrical products. The asymmetry in the phosphate ester molecule is a significant determinant of its physical properties. Symmetrical products are crystalline or waxy solids. Indeed, the only truly symmetrical, pure triaryl phosphate of commercial importance is triphenyl phosphate, which is solid at ambient temperatures and not useful as a fluid base stock. Conversely, controlling the degree of asymmetry produces liquids with varying physical properties, which can be tailored to a variety of application conditions.

As implied by Eq. 2, the asymmetry can be introduced into the molecule by using a mixed feed to the reaction. As long as the reactivity of the phenolic compounds is reasonably close, this method is acceptable, as is the case in production of cresyldiphenyl phosphate, isopropylphenyl, and *t*-butylphenyl phenyl phosphates. Also with tricresyl or trixylenyl phosphates, the similar reactivity of the ortho, meta, and para isomers makes the preparative reaction straightforward.

Asymmetry can also be introduced into the triaryl phosphate molecule by stepwise reaction of the sodium salt of a phenolic alcohol with an intermediate chloridate [13]. The following reaction scheme is one of several possible alternatives:

$$2\mathrm{ROH} + \mathrm{POCl_3} \rightarrow (\mathrm{RO})_2(\mathrm{Cl})\mathrm{P{=}O} + 2\mathrm{HCl} \quad (3)$$

$$\mathrm{R'ONa} + (\mathrm{RO})_2(\mathrm{Cl})\mathrm{P{=}O} \rightarrow (\mathrm{RO})_2(\mathrm{R'O})\mathrm{P{=}O} + \mathrm{NaCl} \quad (4)$$

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The properties of the mixtures prepared by these reactions can be quite similar to those of symmetrical triaryl phosphates with a similar alkyl aryl content.

2. Trialkyl Phosphates

Trialkyl phosphates can be prepared using reactions similar to those used for triaryl compounds. However, because trialkyls are generally less stable than triaryls, the reaction (Eq. 1, phosphorylation of an alcohol) is usually carried out at more moderate temperatures. To drive the reaction to completion, greater excesses of alcohol are needed, and the by-product hydrogen chloride must be removed as rapidly as possible.

The higher molecular weight trialkyl phosphates can be purified by stripping the unreacted alcohol, alkaline washing, and distillation drying, in steps similar to those used for the triaryl processes. The lower molecular weight esters, below tripropyl phosphate, can be isolated only by dry techniques because they are soluble in water.

Because of the inefficiencies of the aliphatic alcohol phosphorylation process, trialkyl phosphates are commercially produced by the reaction of the sodium alkoxide with phosphorus oxychloride:

$$3RONa + POCl_3 \rightarrow (RO)_3P{=}O + 3NaCl \quad (5)$$

In this process, commonly referred to as the alkoxide process, the chlorine values precipitate rapidly as sodium chloride, NaCl. The NaCl can be removed by water washing, with further purification of the phosphate accomplished by distillation under vacuum.

Mixed or unsymmetrical trialkyl phosphates can be produced by using mixed alcohol feeds or by stepwise reaction of the intermediate chloridate with an alkoxide as in Eqs. 3 and 4.

3. Alkyl Aryl Phosphates

The alkyl aryl phosphates, either alkyl diaryl or dialkyl aryl esters, can be made by the reaction of the appropriate purified intermediate alkyl or aryl chloridate with the desired alcohol under reactions and purification techniques similar to those described above. The lower molecular weight dialkyl aryl phosphate esters (e.g., dibutylphenyl phosphate) are apparently best obtained [25] by the preparation of the dialkyl phosphoryl chloride (dialkyl phosphorochloridate) as in Eq. 3, which is purified by distillation under reduced pressure. The chloridate is then reacted with the sodium arylate in water:

$$(RO)_2(Cl)P{=}O + R'ONa \rightarrow (RO)_2(R'O)P{=}O + NaCl \quad (6)$$

The dialkyl aryl esters can then be isolated and purified by the techniques already described.

In the interest of economics, actual commercial processes often vary in some degree from the preceding relatively simple reaction schemes. Such variations often produce mixtures rather than pure products. For example, commercial DBPP may be a mixture containing TPP, TBP, monobutyl- and dibutylphenyl phosphate, giving an average composition and molecular weight of pure DBPP. These factors need to be kept in mind in evaluations of a variety of performance characteristics.

Much of the process development in recent years on the production of the trisubstituted phosphate esters has involved improvements in process efficiency [22–27], including development of continuous process steps [28], which have replaced batchwise operations of some earlier processes.

III. PROPERTIES AND PERFORMANCE CHARACTERISTICS

A. Chemical Properties

Chemical inertness is one of the primary attributes of any lubricant or fluid base stock. The fluid should not react with the metals or other materials from which the mechanical system is

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constructed. Since additives are commonly used, the base stock should not be reactive with or attacked by other classes of chemical compounds.

The trisubstituted phosphate esters, being neutral, have proven chemical stability through many years of practical industrial service over a wide temperature range. They generally do not react with most organic compounds and are excellent solvents for most commonly used lubricant additives. Other aspects of chemical stability for synthetic base stocks—their thermal, oxidative, and hydrolytic stability—are more significant. The following discussion emphasizes these latter properties.

As noted above, most of the commercially important phosphate ester fluids are actually mixtures in which a range of useful properties is achieved through asymmetry. (One major exception is tributyl phosphate, TBP.) To provide the most practical applications data, we emphasize commercially important products in their commercial form. To facilitate the presentation, we use the following abbreviations for commonly occurring fluid/lubricant products:

Triaryl phosphate esters

CDP	cresyl diphenyl phosphate
IPPP	isopropylphenyl phenyl phosphates (triphenyl phosphate, propylated)
TBPP	*t*-butylphenyl phenyl phosphates (triphenyl phosphate, butylated)
TCP	tricresyl phosphate
TPP	triphenyl phosphate
TXP	trixylenyl phosphate

Trialkyl phosphate esters

TBP	tributyl phosphate (tri-*n*-butyl phosphate)
TBEP	tributoxyethyl phosphate
TiBP	triisobutyl phosphate
TOP	trioctyl phosphate (tri-2-ethylhexyl phosphate unless otherwise noted)

Alkyl aryl phosphate esters

DBPP	dibutylphenyl phosphate
EHDPP	2-ethylhexyl diphenyl phosphate
IDDPP	isodecyldiphenyl phosphate

Where appropriate, to further describe the product if it is used commercially as a base stock, the ISO grade number follows the ester designation. For example, IPPP46 defines an ISO 46 phosphate ester base stock derived from isopropyl phenol; TBPP32 defines an ISO 32 base stock made from *t*-butyl phenol.

The information presented below attempts to give a concise and accurate summary of the properties and usefulness of commercial phosphate esters. The early technical development of phosphates has been reviewed [18]. The uses and properties of TBP have been thoroughly reported by Schulz and Navratil [29]. Additional physical and chemical data, directed more toward field use of fluids, is contained in several volumes edited by E. R. Booser [30,31]. Phillips has also authored an in-depth review of physical and chemical properties, handling, and operating procedures directed toward practical field use of phosphate ester fluids and lubricants [32].

1. Thermal Stability

Thermal stability will generally define the temperatures at which a fluid can be used. While in practical operating systems oxygen is usually present, study of the thermal stability in the absence of oxygen gives a clearer picture of the effect of temperature only. For example, localized hot spots at the asperities of a lubricated surface will place thermal stress on the fluid and cause degradation in the absence of oxygen. In practical applications, thermal stability is typically

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Table 1 Relative Thermal Stability of Phosphate Esters Under Nitrogen Atmosphere (ASTM E-537) by Differential Scanning Calorimetry

Phosphate ester	Initiation of decomposition (endotherm) temperature (°C)
TPP	—[a]
TCP	333
TXP	311
CDP	306
TBPP 22–46	338–347
IPPP 22–46	311–314
EHDPP	252
IDDPP	264
TBP	283
TOP	281
TBEP	276

[a] Does not decompose under these conditions.
Source: Ref. 35.

judged in relation to both temperature and time, that is, the shorter the time of exposure at a given temperature, the higher the temperature that can be tolerated.

Over the years, a number of studies [18,33,34] have attempted to define and rank the relative thermal stability of the phosphate esters. The general conclusions from these studies indicate that the triaryls are most stable and the trialkyls the least, with the alkyl aryls intermediate.

A recent attempt to evaluate thermal stability [35] employed thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). ASTM Methods D-3850 and E-537 were used, respectively, except that the samples were tested under nitrogen to eliminate oxidation effects. The DSC method estimates the "onset of decomposition" as the temperature at which an endotherm occurs when the sample is heated at a constant rate of 10°C/min. The TGA method measures the decomposition by determining the weight loss as the sample is heated, and the data are recorded as the temperature at which a given percent weight loss is reached.

In both DSC and TGA techniques, the temperature recorded as the "onset of decomposition" might be influenced by evaporation of the most volatile component if the test fluid is a mixture. Evaporation is endothermic in DSC and will result in weight loss in TGA. This is especially true for compounds such as IPPP and TBPP, which are mixtures of monomeric compounds and can contain appreciable amounts of TPP.

The DSC data in Table 1 show that commercially used triaryl phosphates begin to show an endotherm, whether decomposition or evaporation, over 300°C, well above common operating temperatures. TPP content apparently has little influence on the data, since it did not decompose below 360°C in a similar test conducted in a sealed tube. The three common trialkyls begin to decompose in the 275–285°C range.

The TGA data in Table 2 also show that significant loss does not begin to occur until well above common system operating temperatures. The data on the commercial IPPP and TBPP fluids show the influence of evaporation of TPP, a significant and the most volatile, component present in these base stocks. The data in Tables 1 and 2 support the prior studies regarding the relative stability as well as practical experience developed over the years, namely, that the triaryl

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Table 2 Relative Thermal Stability of Phosphate Esters Under Nitrogen by Thermal Gravimetric Analysis (ASTM D-3850)

Weight loss (%)	Temperature (°C) for TPP	IPPP 22	IPPP 32	IPPP 46	TBPP 46	TCP	TBP	TBEP	TOP
10	261	274	272	265	301	278	154	221	208
20	281	292	294	285	320	298	173	242	231
30	294	304	307	297	333	310	183	254	242
50	310	320	324	313	350	325	196	269	257
75	323	334	339	327	365	325	207	279	268

Source: Ref. 35.

esters are the most thermally stable of the phosphates, more stable than either the trialkyl or alkyl aryl esters.

Several studies [18,36–38] of the pyrolysis of phosphate esters have shown that the decomposition products are unsaturated hydrocarbons and acidic phosphate esters. Results are similar with both the trialkyl and alkyl aryl esters, indicating that the weakest link in the decomposition is the aliphatic carbon–oxygen bond. Again, the triaryl esters are the more stable. Alkylation of the ring in the triaryls tends to reduce the thermal stability but this, in turn, can be affected by the length and branching of the alkyl chain. Overall, all three classes of phosphate esters exhibit sufficient thermal stability for many commercial applications, although the triaryls have achieved the widest use.

2. Oxidative Stability

The oxidative stability of phosphate esters has proven to be quite high and has not been a significant deterrent to their commercial use. Cho and Klaus [39] investigated the oxidative degradation of trialkyl and triaryl phosphates using the apparatus known as the Penn State micro-oxidation tester. The results of this study (Table 3) showed that the triaryl esters are again more stable than the trialkyl esters and that both types, without additives, were more stable than formulated organic ester aircraft engine oil (MIL-L-7808) lubricants.

Table 3 Oxidative Stability of Phosphate Esters[a]

Phosphate ester	Time (min)	Temperature (°C)	Percent of original product: Unoxidized	Oxidized	Evaporated
TBP	5	225	13	6	51
	10	225	19	8	73
TCP	30	225	85	1	14
	60	225	67	2	31
TCP	30	250	57	3	40
TXP	30	250	65	4	31
TCP	15	270	60	5	35
TXP	15	270	55	6	39
DBPP	360	250	77	<1	22
	180	270	81	<1	15

[a] As determined in the Penn State Micro-oxidation Test apparatus [39].

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The study showed no evidence of oxidation of the P—O—C bond, but rather that degradation was dependent on the structure of the alcohol from which the phosphate ester was derived. The higher molecular weight products of the oxidation were shown to be condensation products of the oxidized hydrocarbons.

Some commercially available phosphate ester fluids and base stocks were compared using DSC (ASTM E-537) and TGA (ASTM D-3850) methods in an oxygen atmosphere [40]. These data (Table 4) are consistent with earlier studies. In addition to confirming the superior stability of the triaryl esters, the results show the resistance of TPP to oxidation. Since the onset of oxidation depends on the weakest alkyl chain in the mixture, and commercial mixtures will vary, the authors indicate that a 15–20°C variation in onset temperature could be expected. In the ASTM E-537 test, TPP evaporates before oxidation occurs.

Although alkylation of the ring tends to lower the oxidative stability, there appears to be little difference between adding one or two methyl groups, as in tricresyl and trixylenyl esters. The addition of varying amounts of isopropyl groups also appears to have little effect compared to methyl groups under these conditions. The esters derived from butyl phenol are more stable than those derived from either methyl- or isopropyl phenol.

Based on the thermal stability data, vapor pressure data (see Section III.B, Physical Properties), and other practical operating experience, the triaryl phosphates can be confidently used in systems operating at temperatures up to 135°C for extended periods, and up to 230°C for short periods.

3. Hydrolytic Stability

Phosphate esters can be considered to be the reaction products of an organic alcohol and inorganic phosphoric acid. Like all esterifications, the preparative reaction can be reversed in the presence of water. That is, hydrolysis can occur under the proper conditions. In fact, hydrolysis is the most important consideration in commercial application of phosphate and other organic esters.

As in the thermal and oxidative degradation processes, the hydrolysis reaction will produce acidic products, since it is the —O—C— bond that is attacked:

$$(RO)_3P{=}O + H_2O \rightarrow (RO)_2(OH)P{=}O + ROH \qquad (7)$$

This hydrolysis reaction proceeds stepwise, first yielding the starting alcohol, phenol, or alkyl phenol and the disubstituted phosphoric acid ester.

If the reaction is driven to completion, phosphoric acid and the starting alcohol/phenol will be generated, although lubricant/fluid operating conditions are not harsh enough to allow this to occur to any significant extent. Hydrolysis reactions are acid catalyzed, and thus the hydrolytic degradation can be considered autocatalytic: that is, the acid products of hydrolysis further catalyze the decomposition.

Because hydrolysis is so important in evaluating both product and system performance, numerous studies have been reported. A variety of factors mitigate the ability to compare different studies as well as to evaluate specific results. Test methods often were designed for mineral oils and employ large excesses of water, which tends to exaggerate and accelerate the hydrolysis of esters. Proper attention should be given to the accuracy and precision of the tests as well as the meaning of the results when applying the tests to chemical compounds of different types. As an example, calculations would show that simply extracting the acid value from a typical phosphate ester fluid base stock (0.1–0.3 mg KOH/g), with no hydrolysis, will yield a water layer acidity high enough to fail the typical criteria of 5 mg KOH in the widely used ASTM D-2619 “beverage bottle” test.

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Table 4 Oxidative Stability of Phosphate Esters Under ASTM E-537 (DSC) and D-3850 (TGA) Methods[a]

Phosphate ester	Oxidation onset (°C)	Temperature (°C) at 1% Wt loss	5% Wt loss	10% Wt loss
TBP	175	65	100	115
TiBP	192	84	116	130
TOP	160	60	169	191
TBEP	155	35	145	170
EHDPP	200	90	220	229
IDDPP	165	93	213	235
Triphenyl	—[b]	185	220	235
Tricresyl	215	170	230	260
Trixylenyl	210	225	260	280
IPPP 22[c]	215	200	239	263
IPPP 32[c]	215	201	252	272
IPPP 46[c]	210	202	265	287
IPPP 68[c]	210	218	265	288
IPPP 100[c]	180	224	243	258
TBPP 22[c]	295	213	262	280
TBPP 32[c]	290	222	268	286
TBPP 46[c]	300	227	272	292
TBPP 68[c]	300	230	275	293
TBPP 100[c]	305	234	277	295
Mineral oil[d]	167	155	205	225

[a] Oxygen flow, 75 mL/min; temperature 30–400°C; aluminum sample container. The data represent the range of values obtained on samples of fluids or base stocks of various suppliers.
[b] Does not oxidize under these conditions.
[c] All these products are complex mixtures containing TPP and the respective alkylphenyl phenyl phosphates. Oxidation onset temperature will depend on the weakest alkyl phenol isomer present; the authors found that the data could be expected to vary by ±10°C.
[d] ISO 22 solvent-refined paraffinic neutral oil.
Source: Refs. 30 and 40.

Gamrath, Hatton, and Weesner [18] studied the relationship of hydrolytic stability to the structure of phosphate esters, with emphasis on alkyl diaryl esters, by heating them for 24 hours at reflux with distilled water. The authors concluded that the trialkyl and triaryl esters were generally more stable than the alkyl diaryl esters, although structure had a considerable affect. The data showed that higher molecular weight alkyl chains are more stable than chains of lower molecular weight, that branched chains are more stable than straight chains, and that the alkyl dicresyl esters are more stable than the corresponding alkyl diphenyl esters (Table 5). While esters of all three types have been successfully used as fluid base stocks, only the TBPP and IPPP esters are important today in industrial uses.

In the ASTM D-2619 hydrolytic stability test, the fluid contained in a beverage bottle with a copper strip is rotated slowly at 93°C for 48 hours. The acidity of both the fluid and water layer is determined and the weight loss of the copper strip is measured. Producers' literature

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Table 5 Hydrolytic Stability of Selected Phosphate Esters

Phosphate ester	Acid released per mole of phosphate ester[a]
Tributyl	4.0
Tri-2-ethylhexyl	0.2
Tricresyl	1.2
n-Butyl diphenyl	27.8
t-Butyl diphenyl	7.3
n-Octyl diphenyl	14.6
6-Methylheptyl diphenyl	7.6
2-Ethylhexyl diphenyl	3.6
n-Octyl dicresyl	4.4
2-Ethylhexyl dicresyl	1.7

[a] Expressed as moles of monobasic acid equivalents.
Source: Ref. 18.

[41–43] shows (Table 6) that unstabilized phosphates, especially TXP and the higher viscosity TBPPs, can come very close to passing the typical criteria. When properly formulated, fluids made from TXP, IPPP, and TBPP readily pass the typical criteria.

In the practical application and use of phosphate esters, management of hydrolysis becomes the most important control element. While thermal and oxidative degradations can and do occur, hydrolysis from moisture contamination, accelerated by heat and acidic by-products, becomes the dominant cause of deterioration of phosphate ester fluids. Conversely, if hydrolysis is kept under control, the phosphate ester fluid or lubricant can remain useful in commercial equipment for years without replacement (see Section III.E, below).

Perhaps more useful criteria are shown by previously unpublished data [44] generated using ASTM D-2619 on multiple samples of commercial products and repeated test runs on each sample. The study showed that broad variation in the data can be expected among different operators, and within samples with the same operator from slight procedure variations within the test protocol. However, the summarized and averaged data shown in Table 7 provided a clear ranking of the various esters and confirmed (a) the relative stability of the cresylic acid esters TCP and TXP, (b) the instability of TPP and the consequent improvement in stability of the IPPP and TBPP series as the degree of alkylation and molecular weight increases, and (c) the positive response of phosphate esters to standard additives.

B. Physical Properties

Phosphate esters commonly used as fluid and lubricant base stocks are all monomelic molecules and all contain the phosphorus–oxygen–carbon (P—O—C) bond system as the central skeletal structure. While this P—O—C bond structure influences the basic properties, the organic moiety will determine most of the variation in physical properties exhibited by this class of compounds. Manufacturers achieve the range of properties mainly through variation of the size and number of the alkyl chains involved, whether alone in the trialkyl esters or attached to the aryl ring in the triaryl esters.

In trialkyl esters, as the molecular weight increases, viscosity, boiling point, and pour points

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Table 6 Hydrolytic Stability of Some Commercial Phosphate Ester Hydraulic Fluids and Base Stocks (ASTM D-2619)

Phosphate ester fluid	Increase in fluid acidity (mg KOH/g)	Increase in water acidity (mg KOH)	Copper weight loss (mg/cm^2)
TCP	0.095	9.1	0.30
TXP	Nil	Nil	0.03
TBPP 46	0.045	6.17	0.18
TBPP 68	0.09	8.98	0.34
TBPP 100	0.20	11.2	0.45
TBPP 32 Gas turbine oil	0.0	4.21	0.0
TBPP 46 MIL H 19457d fluid	0.03	2.71	0.05
IPPP 46 Industrial fluid	0.05	1.4	0.05
IPPP 100 Compressor oil	0.12	1.3	0.04
Standard criteria	0.2 max	5.0 max	0.3 max

Source: Refs. 41–43.

Table 7 Hydrolytic Stability of Phosphate Esters (ASTM D-2619)

Phosphate ester	Average water acidity (mg KOH/g)	Copper weight loss (mg/cm^2)
Unformulated esters		
TCP	12	1.1
TXP	7	0.5
IPPP 22	37	12
IPPP 32	24	2
IPPP 46	14	0.4
IPPP 68	9	0.1
TBPP 22	25	0.7
TBPP 46	10	0.6
TBPP 100	3	0.5
TBEP	250	0.3
TBP	85	1
TOP	8	>0.1
Formulated fluids		
TXP	1	0.1
TBPP 32	8	0.1
TBPP 46	3	0.1
Standard criteria	5.0	0.3

Source: Ref. 44.

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or freezing points increase and melting point decreases. The triaryl esters present a somewhat different situation, in that the simplest molecule, triphenyl phosphate, is a solid at ambient temperature, melting at about 49°C. As alkyl side chains are introduced, often introducing asymmetry at the same time, the melting point at first declines, giving useful liquids at ambient conditions; for example, cresyl diphenyl, tricresyl, trixylenyl, and many other alkylphenyl phenyl phosphates are liquids. Within the series of liquids, behavior generally becomes normal; that is, viscosity, pour point, and boiling point increase as molecular weight increases.

The following sections emphasize the properties of the important fluid and lubricant base stocks, with other compounds included to illustrate trends or changes. Recent developments in environmental and other areas have generated greater interest in trialkyl esters TBP, TOP, and TBEP for industrial base stocks.

1. Vapor Pressure and Boiling Point

Vapor pressure and boiling point (or range) play a significant role in the useful operating temperature range of a fluid. Phosphate ester base stocks generally have very high boiling points compared to other organic liquids with similar viscosities, as shown in Table 8. The trialkyls have the lowest boiling points; tri-*n*-butyl phosphate, used in aircraft and low temperature formulations, boils at about 284°C.

The triaryl esters most widely used in industrial fluids have boiling points above 400°C at atmospheric pressure and over 250°C at 10 mmHg. All the triaryl base stocks, except for the ISO 100 grades, have a significant amount of triphenyl phosphate in them, and all are mixtures of isomers. Commercial products are more correctly described as having boiling ranges, which are generally between 220 and 270°C at 4 mmHg.

Vapor pressure of phosphate esters has been calculated with the Clausius–Clapeyron equation [45]:

$$\log P = \frac{A}{T} + B \tag{8}$$

where P is the vapor pressure, T is the temperature and A and B are constants. Table 9 contains values for A and B along with the vapor pressures calculated from several forms of Eq. 8. The commercial triaryl phosphate base stocks (i.e., the IPPP and TBPP esters, ISO grades 22–100) generally have vapor pressures below 1 mmHg at 210°C—extraordinarily low for monomeric materials. The phosphate ester base stocks used commercially are less volatile than mineral oils of similar viscosity and, when properly chosen, will provide excellent performance at most ambient working conditions as well some low pressure applications.

2. Viscosity

Viscosity and its variation with temperature significantly influence the design of equipment and the choice and performance of a lubricant/fluid. So much has been written on this subject that additional discussion is not presented here. Among numerous other books and articles, *The Handbook of Lubrication, Theory and Practice of Tribology* [46] is an excellent source.

The viscosity of the commercially important phosphate esters falls in a wide and useful practical range (Table 10). The triaryl esters are marketed in ISO grades ranging from ISO 22 to ISO 100. Pour points of the triaryl esters generally fall between −10 and 20°C. Viscosity index (VI) of the triaryl esters is relatively poor, generally well below 100 and often near zero.

The trialkyl esters have lower viscosity and pour points, and superior VIs, compared to the triaryls. The VIs of some trialkyl esters are near 100, comparable to paraffinic mineral oils.

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Table 8 Boiling Point and Heat of Vaporization of Phosphate Esters

	Boiling point (°C)		Latent heat of vaporization (kJ/mol)
	At 760 mmHg	At 10 mmHg	
Trialkyls			
Methyl	196		
Ethyl	215		
n-Propyl	252		
n-Butyl	284	155	61.4
Isobutyl	264	137	62.9
2-Ethylhexyl	384	211	66.6
Butoxyethyl	320	220	
Triaryls			
TPP	413	254	81.5
TCP	427	271	86.6–110.8
TXP	402	276	
CDP	414	265	66.2
IPPP 22	365	255	90–110
IPPP 32	385	258	90–110
IPPP 46	396	262	90–110
IPPP 68	407	267	90–110
IPPP 100	415	272	90–110
TBPP 32	402	260	90–110
TBPP 46	416	269	90–110
TBPP 68	424	270	90–110
TBPP 100	435	271	90–110
Alkyl aryls			
EHDPP		240	69.3
IDDPP		249	
DBPP	325	185	93.8

Source: Refs. 19, 30, 31, 41, 42.

Figure 1 summarizes the viscosity/temperature profiles of commercial phosphate ester hydraulic fluids. The IPPP and TBPP Triaryl Phosphates products are combined for the purpose of simplifying the figure. The individual ISO grades of each class behave quite similarly as temperature changes, and are represented approximately by the lines shown. Suppliers' literature [41–43] and Table 10 provide more specific data points.

The useful operating range of either the alkyl or aryl family of esters can be extended by blending chemically or physically. That is, alkyl aryl esters (chemical "blends") can be prepared, or a trialkyl and a triaryl ester can be physically mixed, to give viscosities, pour points, and VIs better than those of the individual components. Commercially available polymers also can be used to improve the VI of phosphates. The aircraft hydraulic fluid products [47–50] are a primary example of the practical application of these techniques. These products (Table 11), which are 100% phosphate ester based with a vi improver, have pour points typical of the trialkyl phosphates and high temperature viscosities more typical of the triaryl esters.

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Table 9 Calculated Vapor Pressure of Phosphate Esters[a]

	Vapor pressure (mm Hg)				Constants		
	70°C	110°C	210°C	310°C	*A*	*B*	Equation[b]
Triaryl phosphates							
IPPP 22	3.02×10^{-6}	2.4×10^{-4}	0.562	92.14	14,369.5	29.164	*x*
IPPP 32	3.05×10^{-5}	1.0×10^{-3}	0.921	70.34	12,217.2	25.203	*x*
IPPP 46	7.77×10^{-6}	4.0×10^{-4}	0.441	43.84	12,962.0	26.008	*x*
IPPP 68	4.25×10^{-5}	1.0×10^{-3}	0.743	45.09	11,569.1	23.647	*x*
IPPP 100				33.0			
TBPP 32	1.0×10^{-4}	3.0×10^{-3}	1.12	56.15	11,038.1	22.956	*x*
TBPP 46	7.69×10^{-5}	2.0×10^{-3}	0.831	41.25	11,000.8	22.584	*x*
TBPP 68			0.06	45.1			
TBPP 100			0.02	31.2			
TPP	4.68×10^{-4}	9.2×10^{-3}	1.8	59.9	4,253.0	9.07	*y*
TCP	8.62×10^{-5}	2.0×10^{-3}	0.768	35.12	10,771.2	22.029	*x*
TXP	7.05×10^{-6}	3.6×10^{-4}	0.38	37.4	12,874.3	25.687	*x*
CDP	2.4×10^{-4}	5.4×10^{-3}	1.39	52.85	10,258.7	21.559	*x*
Trialkyl phosphates							
TBP	0.1325	1.398	91.42		7,735.0	20.53	*x*
TiBP	0.256	2.648	157.6		3,283.1	8.995	*y*
TBEP	6.2×10^{-5}	3.4×10^{-3}	4.35	472.8	5,734	12.51	*y*
TOP	1.1×10^{-2}	0.1251	9.41	160.8	3,471.0	8.16	*y*
Alkyl aryl phosphates							
EHDPP		0.2[c]	1.6[d]				
IDDPP		<0.1[c]	0.5[d]				
DBPP	0.0205	0.2698	26.17	528.2	3,674.8	11.151	*z*

[a] Calculated from the Clausius–Clapeyron equation form in the right-most column.
[b] Equation *x*: $\ln P = [-A/T] + B$ (where $T = K$, P = mmHg)
Equation *y*: $\log_{10} P = [-A/T] + B$ (where $T = K$, P = mmHg)
Equation *z*: $\log_{10} P = [-A/T] + B$ (where $T = K$, P = pascals) (133.3 mmHg/Pa)
[c] At 150°C.
[d] At 200°C.
Source: Refs. 29–31, 40, 42, 44.

The viscosity index of straight triaryl esters can also be improved with typical polymeric VI improvers. Acrylic, styrenic, and other polymers have been used successfully [30,49,50].

Phosphate esters possess a correlative advantage compared to their low viscosity index, that is, their excellent viscosity stability. The products are monomeric rather than polymeric, and they are based on stable aromatic rings and/or relatively short alkyl chains. Thus, there is little in the molecular structure susceptible to the shearing forces normally found in hydraulic systems. This stability has been demonstrated (Fig. 2) in a field trial [51] of an electrohydraulic control fluid in a 300 MW steam turbine. The viscosity remained virtually unchanged for more than 10 years and remained well within equipment manufacturer operating specifications. The original fluid remained in the system during the entire period plotted in Fig. 2 with only minor additions of makeup fluid.

Phosphate esters can also be blended with other base stocks, synthetic or petroleum, to provide still broader properties [52,53].

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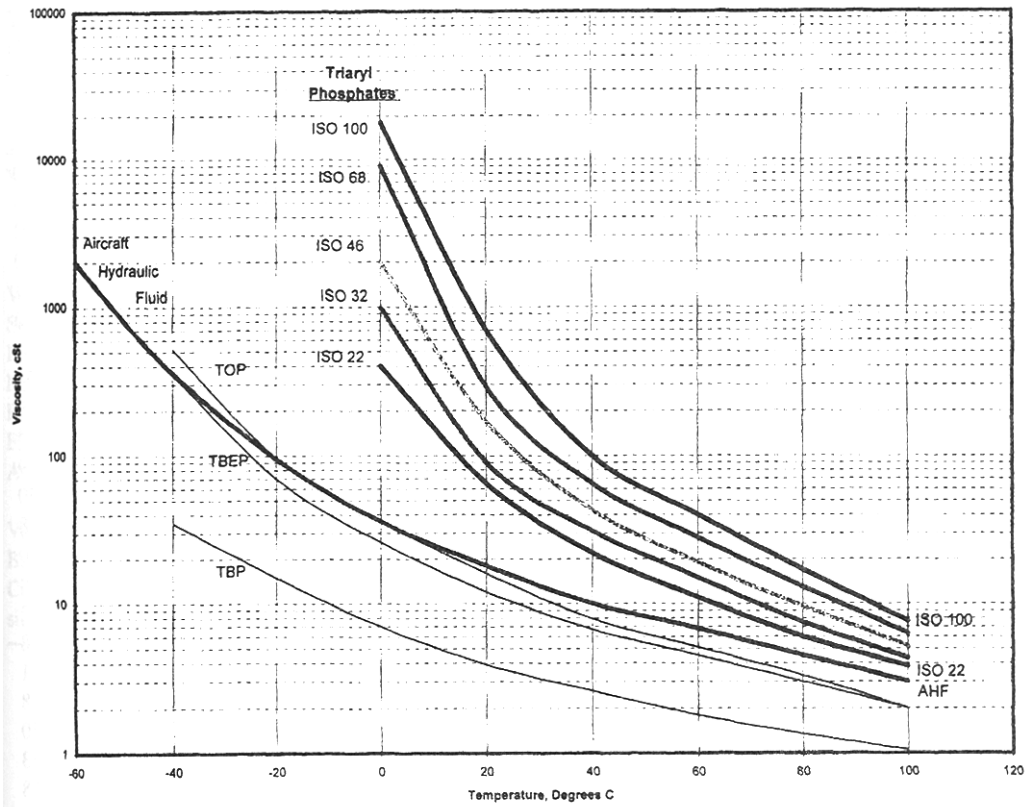

Figure 1 Viscosity–temperature relationship for some commercial phosphate esters.

As equipment is designed to operate at higher pressures, the variation of viscosity with pressure can become important. Table 12 shows the variation of viscosity with pressure of an isopropyl phenol based ISO 46 commercial fluid [41].

3. Other Properties

A variety of other physical properties must be considered in the use of lubricants and the design of equipment. Tables 13 through 15 summarize data from a variety of sources, including suppliers' technical literature [19,30,41–43].

Density and Specific Gravity (Table 13). The unit weight of a fluid influences flow characteristics, the weight of a system, and other factors considered in equipment design. Triaryl phosphates are more dense than the trialkyl esters. Within both families, the density and specific gravity decrease as the molecular weight increases. The alkyl aryl esters have intermediate values.

Phosphate esters are more dense than water and mineral oils. In a wastewater treatment system, for example, petroleum oil, being less dense than water, rises to the surface and can be skimmed. Phosphate esters, being denser than water, collect in low points of the system. Likewise, in a hydraulic system running on a triaryl phosphate ester fluid, significant levels of water from leakage or accidental contamination collect on the surface of the fluid, usually in the sump.

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Table 10 Viscometric Properties of Phosphate Esters

Phosphate ester	Viscosity (cSt) 0°C	20°C	40°C	100°C	Viscosity index	Pour point (°C)
TBP	7	3.9	2.6	1.05	118	< −90
TiBP	10	4.9	3.0	1.12		< −90
TBEP	26	12	6.7	2.0	90	−90
TOP, tri-2-ethylhexyl	36	16	7.9	2.0	145	−90
Tri-*n*-octyl			8.4	2.5	148	−1
DBPP			4.45	1.2		< −70
Di-2-ethylhexyl, phenyl			8.6	2.2	67	
EHDPP	61	25.6	8.6	2.25		−54
IDDPP		19.6		3.0		−50
CDP	220	44	16.5	3.2	35	−34
Tri(3-isopropylphenyl)			42.7	5.53		59
Tri(4-isopropylphenyl)			53.6	6.14		50
TCP	1,000	76	24	3.8	0	−28
TXP	1,700	170	43	5.2	<0	−20
IPPP 22	400	65	22	3.8	25	−28
IPPP 32	990	76	31	4.3	20	−22
IPPP 46	1,600	140	43	5.2	10	−18
IPPP 68	7,600	280	65	6.3	0	−11
IPPP 100	14,400	550	103	6.6	<0	−8
TBPP 22	449	72	24	4.0	35	−30
TBPP 32	1,500	90	31	4.6	25	−23
TBPP 46	2,500	160	43	5.3	15	−18
TBPP 68	9,000	290	65	6.3	5	−11
TBPP 100	18,000	700	100	7.8	<0	−5
Aircraft fluid	36	18	10	3.0	260	< −62

Source: Refs. 18, 29, 31, 40–42, 47.

Thermal Properties. Like density, specific heat (C_p) is a characteristic property of a material and is significant in the design of heating or cooling capacity of a system. While the specific heat value of a phosphate ester varies with temperature, the values lie within a relatively narrow band over a broad temperature range, as shown in Table 14.

The thermal conductivity of most triaryl phosphate fluids is approximately 0.46 kJ/h/m/°C in the temperature range 40–90°C. The coefficient of thermal expansion between 25 and 75°C of these fluids is 6.9×10^{-4} $cm^3/cm^3/°C$. While some variation may exist between laboratories and among the various esters, the values above are representative of the entire class of commercial triaryl phosphate fluids. Phosphate esters generally are better heat transfer agents than mineral oils.

Compressibility and Bulk Modulus. Compressibility of a fluid, or its reciprocal, bulk modulus, is an important factor in hydraulic system performance. A compressible fluid will result in sluggish operation, greater energy consumption, and heat buildup. Phosphate esters are less compressible than petroleum oils (Table 15) and thereby provide rapid hydraulic response and efficient operation.

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Table 11 Typical Physical Properties of Phosphate Ester Aircraft Hydraulic Fluid

	Type IV [47]	Type V [48]
Viscosity (ASTM D-445), cSt		
At −65°C	1363	1911
At 38°C	10.6	9.19
At 99°C	3.3	3.13
Viscosity index	260	
Specific gravity 25/25°C	0.995	0.977
Pour point (ASTM D-97), °C	< −62	−62
Neut. no. (ASTM D-974)	0.03	0.04
Flash point (ASTM D-92), °C	178	164
Fire point (ASTM D-92), °C	185	183
Autoignition temperature (ASTM D-2155), °C	427	482
Vapor pressure at 100°C, mmHg		7.7
Bulk modulus	262,000	211,000
Coefficient of thermal expansion, V/V/°F	4.97×10^{-4}	4.6×10^{-4}

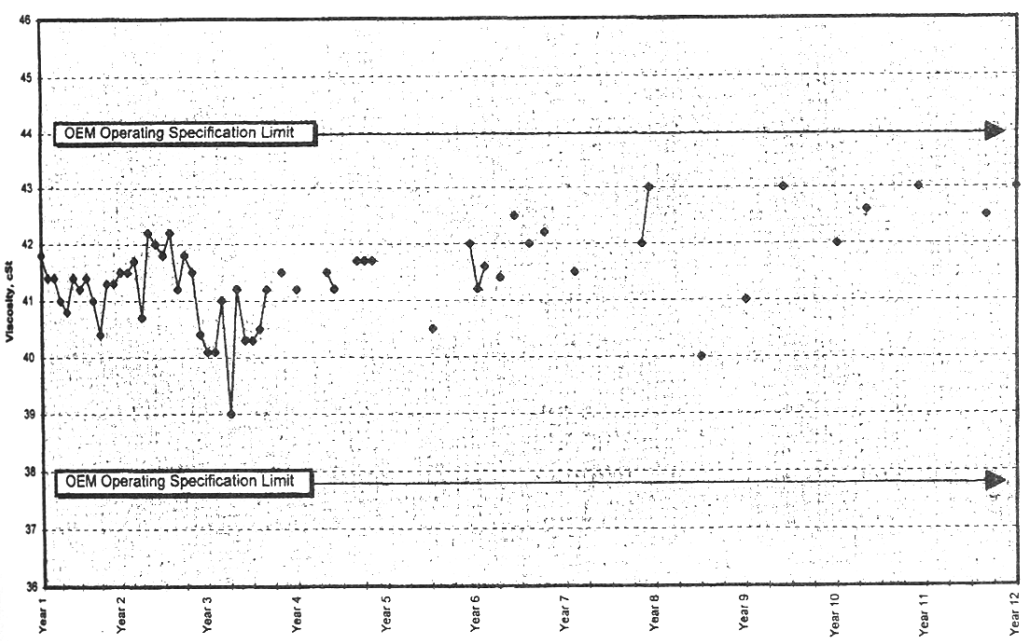

Figure 2 Viscosity stability of TBPP 46 phosphate ester hydraulic fluid in actual commercial use.

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Table 12 Viscosity–Pressure Relationship of a Phosphate Ester ISO 46 (IPPP 46) Hydraulic Fluid

	Viscosity (cP) at		
Pressure	37.8°C	71°C	104°C
0	51.8	11.7	4.9
138	70.8	14.6	5.9
276	96.8	18.2	7.0
414	132	22.7	8.4
552[a]	185	29	10.5
689[a]	260	36	12
827[a]	350	45	15

[a] Extrapolated data.
Source: Ref. 41 except as noted.

Table 13 Specific Gravity of Phosphate Esters

Phosphate ester	Specific gravity at 20/20°C
Trialkyls	
TOP	0.92
n-Octyl	0.915[a]
TBP	0.980
TiBP	0.965
TBEP	1.020
Alkyl aryls	
DBPP	1.04
EHDPP	1.09
IDDPP	1.07
Triaryls	
CDP	1.195
TCP[b]	1.172
TXP[b]	1.142
IPPP 22	1.175
IPPP 32	1.151
IPPP 46	1.130
IPPP 68	1.121
IPPP 100	1.140
TBPP 22	1.180
TBPP 32	1.165
TBPP 46	1.155
TBPP 68	1.145
TBPP 100	1.135

[a] At 25/25°C.
[b] Typical commercial product, mixed isomers.
Source: Refs. 19, 30, 41–43.

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Table 14 Specific Heat of Phosphate Esters[a] Between 60 and 150°C

	Specific heat C_p (J/g/K)		
Phosphate ester	25°C	60°C	150°C
TBP	1.4	1.58	2.04
TiBP	—	2.23	—
TBEP	2.0	2.17	2.2
TOP	—	1.97	2.2
EHDPP	—	1.76	—
TPP	1.7	1.98	2.25
TCP	1.45	1.85	2.13
TXP	1.5	1.66	1.88
CDP	1.45	1.89	2.6
IPPP 22	1.5	1.93	2.33
IPPP 32	1.5	1.75	1.99
IPPP 46	1.6	1.70	1.97
IPPP 68	1.6	1.84	2.09
IPPP 100	1.6	1.85	2.10
TBPP 22	1.5	1.78	2.10
TBPP 32	1.5	1.78	1.85
TBPP 46	1.6	1.87	2.11
TBPP 68	1.6	1.69	1.86
TBPP 100	1.7	1.94	2.09

[a] Determined by differential scanning calorimetry in an unpurged atmosphere under ASTM D-3947-80.
Source: Ref. 30.

Table 15 Bulk Modulus and Compressibility of an IPPP 46 Phosphate Ester Hydraulic Fluid at 37.8°C

Pressure (bar)	Bulk modulus (bar × 10^4)	Compressibility ($bar^{-1} \times 10^{-5}$)
69	1.95	5.13
103	1.97	5.08
138	1.99	5.02
207	2.03	4.93
276	2.09	4.78
344	2.12	4.71
689	2.34	4.27
1034	2.53	3.95

Source: Ref. 41.

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C. Performance Properties

Fire resistance and lubrication characteristics represent the most important performance parameters driving the use of phosphate esters in industrial systems. Although there is variation within the several families of phosphates, these two critical properties are inherent in the phosphate ester molecule: phosphate esters are excellent lubricants and the most fire resistant of the moderately priced synthetic anhydrous fluids/lubricants.

1. Flammability

Combustion, or fire, is the rapid vapor phase reaction of a fuel with oxygen. Ignition and subsequent burning of any given material depend on a variety of chemical and physical properties of the material and the environment surrounding it. Ease of ignition is influenced by thermal and oxidative stability, vapor pressure, molecular weight, heat of vaporization, and similar factors related to molecular content and structure. To maintain combustion after ignition, there must be sufficient oxygen and enough heat released to vaporize the fuel.

The resistance to ignition and burning, normally termed *fire resistance* in the fluids/lubricants field, can be measured by a variety of methods. Techniques have been developed to provide laboratory screening methods as well as simulation of practical industrial crisis situations. These and many other tests fall into one of four categories that attempt to measure either bulk fluid ignition, ignition on a hot surface, ignition of sprays, or ignition when adsorbed on a substrate. Table 16 lists the most important tests that have been developed and accepted worldwide.

Representative fire, flash, and autoignition temperatures are presented in Table 17. It is clear from fire resistance data reported in suppliers' technical literature, as presented in Table 18, that phosphate esters readily pass all the commonly specified tests.

An important distinguishing characteristic of the phosphates esters, which is derived from the presence of phosphorus in the molecule as well as the bond structure, is the heat of combustion. The triaryl phosphates have heats of combustion below 7800 kcal/kg [31,42], whereas

Table 16 Standard Fire Resistance Test Methods

Test	Method and source
Fire point	ASTM D-92
Flash point	ASTM D-92
Autoignition temperature	ASTM E-659[a]
Spray ignition	Factory Mutual Research Corp., Standard 6930 (through 1995); also 7th Luxembourg Report, Sections 3.1.1 and 3.1.2
Spray flammability parameter	Factory Mutual Research Corp. Standard 6930 (1996)
Stabilized flame heat release	7th Luxembourg Report, Section 3.1.3
Hot surface ignition (hot channel)	Factory Mutual Research Corp., Standard 6930
Hot manifold	Federal test method FTMS 791C, Method 6053.1 CETOP[b] RP65H
Molten metal	Several proprietary tests on lead, aluminum, etc.
Wick ignition	7th Luxembourg Report, Section 3.2.1
Linear flame propagation	ASTM D-5306
Compression ignition	U.S. Navy, MIL-H-19457d

[a] Data developed using earlier versions ASTM D-286 and D-2155 continue to be quoted in trade and other literature. Both these methods apparently gave values that are 25–50°C higher than the current method (E-659) apparently because of different test vessel geometry and volume.
[b] CETOP = Comite European des Transmissions Olehydrauliques et Pneumatiques.

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Table 17 Flash Point, Fire Point, and Autoignition Temperature of Phosphate Esters

Phosphate ester	Temperature data (°C)[a]		
	Flash point (COC)[b] ASTM D-92	Fire point ASTM D-92	Autoignition temperature ASTM E-659
TBP	165	182	400
TiBP	155	170	476
TOP	190	240	375
TBEP	190	230	260
DBPP	170		>430
EHDPP	224	238	
IDDPP	240	260	
TPP	224	310	635
CDP	255	340	620
TCP	225	340	600
TXP	255	340	540
IPPP 22	255	335	570
IPPP 32	255	335	545
IPPP 46	255	335	500
IPPP 68	255	335	490
IPPP 100	255	335	490
TBPP 22	240	340	590
TBPP 32	255	350	545
TBPP 46	255	350	535
TBPP 68	255	350	525
TBPP 100	255	350	520

[a] The data can vary as follows: flash point, ±5°C, fire point and autoignition temperature, ±10°C. The range can represent differences resulting from reproducibility and repeatability of the test as well as differences in product tested such as isomer mixture and supplier.
[b] COC = Cleveland Open Cup.
Source: Refs. 29, 41–43.

mineral oils and other synthetic hydrocarbons are in the area of 9500 kcal/kg. The low heat release does not support combustion, and phosphate esters are self-extinguishing when the source of ignition is removed.

The fluids/lubricants industry has recognized shortcomings in certain fire resistance tests, many of which were designed to measure properties of specific fluids and often failed to adequately define or discriminate among an ever widening array of fluids. Recently, in both the United States and Europe, tests have been developed [54,55] in attempts to more clearly define the hazard presented by sustained combustion as well as ease of ignition. These tests attempt to measure the heat released during combustion and the ability to sustain a flame under typical spray conditions.

Until 1995, commercial industrial phosphate ester fluids were classified as HF-D type fluids and as less flammable fluids, group II, in the Factory Mutual Research Corporation rating system [56]. Under the new standards adopted during 1996–1997, Factory Mutual classifies fluids according to a calculated spray flammability parameter (SFP). Phosphate esters and water glycol fluids are classified as class 1, least flammable, with an SFP $<20 \times 10^4$. The Luxembourg Protocol, adopted in 1996, measures an ignitibility factor and classifies fluids from A (= least

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Table 18 Performance of Commercial Phosphate Ester Hydraulic Fluids in Fire Resistance Tests

Test	IPPP 32–68 fluids	TBPP 32–68 fluids	TXP 46 fluid	Test criteria
Fire point (ASTM D-92), °C	325–345	330–360	340	None
Flash point (ASTM D-92), °C	250–260	250–260	255	None
Autoignition temperature, °C	490–570	515–595	540	None
Spray flammability (Factory Mutual)	Pass	Pass	Pass	Self-extinguishes < 10 s
Hot manifold at 704°C (Factory Mutual)	Pass	Pass	Pass	No flashing or burning on tube
Spray flammability factor (Factory Mutual)	Class I	Class I	Class I	Class I = SPF $< 20 \times 10^{-4}$
Hot channel	No ignition	No ignition	No ignition	No ignition
7th Luxembourg ignitability factor	Group E	Group E	Group D	
Wick ignition	Pass	Pass	Pass	Self-extinguishes < 10 s
Molten metal at 815°C	No ignition	No ignition	No ignition	No ignition
Spark ignition	No ignition	No ignition	No ignition	No ignition
Compression ignition ratio (MIL-H-19457d)	41:1	42:1	42:1	>41:1

Source: Refs. 31, 32, 41, 42.

flammable: e.g., oil-in-water emulsions) to H (= most flammable: e.g., mineral oil). Triaryl phosphate ester fluids (unblended) fall into in group D or E in this system.

2. Lubricity

Phosphate esters have proved to be excellent lubricants in practical applications over many years. A number of early studies of phosphate esters [4–6,57–59] led to their use as antiwear additives and defined the mechanism of their lubrication performance. Phosphate esters provide boundary lubrication by reacting with ferrous metal surfaces to form iron phosphides and iron phosphates. These lower melting compounds (at times called eutectics or alloys) are deformed by plastic flow and fill in low spots between asperities on the surface, thus increasing the area of contact and reducing pressure points. The phosphate film is sheared under friction and thereby preserves the integrity of the lubricated surface.

Laboratory data developed on commercial fluids, such as those presented in Table 19 (four-ball wear) and Table 20 (vane pump test), corroborate the practical lubricant performance. The laboratory data show equal or lower rates of wear than those obtained with petroleum oils and other synthetic fluids.

3. Corrosion

Phosphate esters are generally not corrosive to common metals used in hydraulic and other systems. This reliability is best illustrated by performance of a number of commercial fluids and lubricants in the corrosion/oxidation test FTMS (Federal Test Method) 5308.

Performance data of several phosphate ester products are presented in Tables 21 and 22. It should be kept in mind that the decomposition products of thermal or hydrolytic reactions are acidic and can be corrosive to metals. Copper and copper-bearing alloys will typically be the first metals attacked in such situations, and nitrogen-containing, metal-passivating com-

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Table 19 Four-Ball Wear Tests (ASTM D-4172) of Phosphate Ester Fluids[a]

Fluid	Wear scar diameter (mm)
Formulated fluids	
IPPP 46 industrial fluid	0.58–0.64
IPPP 100 compressor lube	0.54–0.60
TBPP 32 gas turbine oil	0.58–0.64
TBPP 46 MIL H 19457 fluid	0.54–0.60
Low temperature hydraulic fluid (alkyl aryl blend)	0.60–0.70
Aircraft hydraulic fluid	0.60–0.70
Unformulated base stocks	
TBP	0.80–0.85
TiBP	0.95–1.10
TOP	0.90–0.94
TBEP	0.80–0.85
TCP	0.58–0.64
TXP	0.58–0.64
CDP	0.58–0.64
IPPP 22	0.64–0.68
IPPP 46	0.58–0.64
IPPP 100	0.54–0.60
TBPP 22	0.60–0.64
TBPP 46	0.54–0.60
TBPP 100	0.52–0.58

[a] At 40 kg load, 1200 rpm, for 1 hour at 75°C.
Source: Refs. 31, 32, 41, 42, 47.

Table 20 Performance of Phosphate Ester Fluids Vane Pump Wear Test (ASTM D-2882)

Fluid	Duration (h)	Temperature (°C)	Weight loss (mg)		
			Ring	Vane	Total
IPPP 22	100	53	3.6	14.5	18.1
	250	53	6.5	15.6	22.1
IPPP 32	100	60	2.5	34.8	37.3
	250	60	2.6	36.7	39.3
IPPP 46	250	66	8.2	8.5	16.7
IPPP 68	100	72	3.7	2.0	5.7
	250	72	5.4	3.3	8.7
TBPP 32	100	66	2.0	5.4	7.4
TBPP 46	100	66	4.3	8.5	12.8

Source: Refs. 31, 32, 41, 42.

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Table 21 Performance of Phosphate Ester Aircraft Hydraulic Fluid in Standard Tests

	Results	Industry standard
Thermal stability at 121°C, 168 h, 0.2–0.3% water		
Metal weight change, mg/cm²		
Steel	−0.06	+0.3 max
Magnesium	0.54	+5.0 max
Copper	0.05	+0.5 max
Cadmium-plated steel	0.05	+0.3 max
Aluminum	0.02	+0.2 max
Total acid number change, mg KOH/g	−0.03	+0.1 max
Viscosity change, cSt		
At 38°C	0.53	+1.0 max
At 99°C	0.10	+0.3 max
Corrosion, hydrolysis, and oxidation stability at 82°C, 168 h, 0.8% water		
Metal weight change, mg/cm²		
Steel	0.01	+0.1 max
Magnesium	0.00	+0.2 max
Copper	−0.02	+0.4 max
Cadmium-plated steel	−0.01	+0.4 max
Aluminum	−0.015	+0.1 max
Total acid number change, mg KOH/g	0.065	+0.3 max
Viscosity change, cSt		
At 38°C	0.08	+3.0 max
At 99°C	0.07	+1.0 max
Four-ball wear test scar diameter, mm		
At 4 kg load	0.21	0.45 max
At 10 kg load	0.34	0.50 max
At 40 kg load	0.65	0.55–0.75
Flammability tests		
Pipe wick (cycles)	34	25 min
Hot manifold at 794°C	No flame	No flame
Low pressure spray	Self-extinguishing	Self-extinguishing

Source: Ref. 47.

pounds, such as benzotriazole, can be included in the phosphate fluid formulation. Maintenance of acid number (TAN) at recommended levels (<0.3 mg KOH/g) can also serve to avoid such potential problems.

4. Solvent Properties

Most phosphate esters are good solvents for other organic compounds including hydrocarbons, alcohols, esters, ketones, and other relatively nonpolar materials. They are widely used as plasticizers for vinyl, cellulosic, and other resins.

This strong solvency can be a benefit in that phosphates can be easily formulated with additives and other base stocks. In addition, phosphate esters used as a cosolvent can improve the solubility of additives, such as metal passivators and antioxidants, in mineral oil and poly (α-olefin) base stocks [60] while providing antiwear, seal swell, and metal passivation performance.

Solvent power also can be a source of problems, as demonstrated by the poor compatibility

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Table 22 Performance of Industrial Phosphate Ester Hydraulic Fluids in Corrosion/Oxidation Test (Federal Test Method FTMS 5308.6)

Properties	Limits	IPPP 32 Gas turbine oil	IPPP 46 Industrial hydraulic fluid	TBPP 46 MIL-H-19457d fluid	IPPP 100 Compressor oil	Low temperature hydraulic fluid[a]
Conditions						
hours		72	72	72	168	72
°C		175	175	175	150	175
Total acid number increase, mg KOH/g	2.0 max	0.4	0.16	1.8	1.0	0.14
Viscosity change, %	−5% to +10%	2.3	1.7	13	8.1	7.4
Metal weight change, mg/cm^2						
Copper	±0.4	−0.007	0.015	0.051	0.01	−0.015
Steel	±0.2	0.029	−0.036	0.007	Nil	−0.007
Magnesium	±0.2	0.015	−0.029	0.015	0.02	Nil
Aluminum	±0.2	0.015	−0.029	Nil	−0.02	Nil
Silver	±0.2	Nil	−0.022	−0.095	0.02	−0.007
Pass/fail		Pass	Pass	Pass	Pass	Pass

[a] Alkyl aryl blended product.
Source: Refs. 30, 31, 41, 42.

with a number of common coatings, seals, and hose materials. Care is required in choosing materials of construction (see Section III.E, below). In systems where phosphate esters replace other fluids, phosphates can be very effective in removing residual sludge and other deposits from internal equipment parts. Preflushing the system or the proper use of filters should be considered in such cases.

5. Additive Response

Being good solvents, phosphate esters are compatible with a wide variety of commonly used lubricant additives such as metal passivators, antioxidants, and VI improvers [49,50,59,61–66]. Additives are not always needed; at least one major supplier of hydraulic fluids claims excellent performance in typical industrial applications without any additives to the products.

In some specialized applications, such as aircraft fluids (Table 20) and turbine lubricants [64–66], additives are used and the response of phosphate ester to them is quite good.

Where additives are needed or desirable, triazoles are typically effective metal passivators, acrylate and methacrylate polymers are excellent VI improvers, hindered phenols act as antioxidants, and silicones can be used as antifoam agents, although they may cloud the fluid.

6. Chemical Stability

An earlier section described the hydrolytic and oxidative reactivity of the phosphate esters. While it is important to understand the theory and mechanisms of these reactions, it is equally important that satisfactory performance in many applications has been well demonstrated. Figure 2 shows the excellent viscosity stability, and thus the lack of chemical reactivity, of an ISO 46 electrohydraulic control fluid in field performance.

Since acidic products are formed from both the hydrolysis and oxidation of the esters, a rising acid number would indicate ongoing degradation of the fluid. Acid number data collected over a 10-year period in the steam turbine system mentioned previously clearly demonstrates

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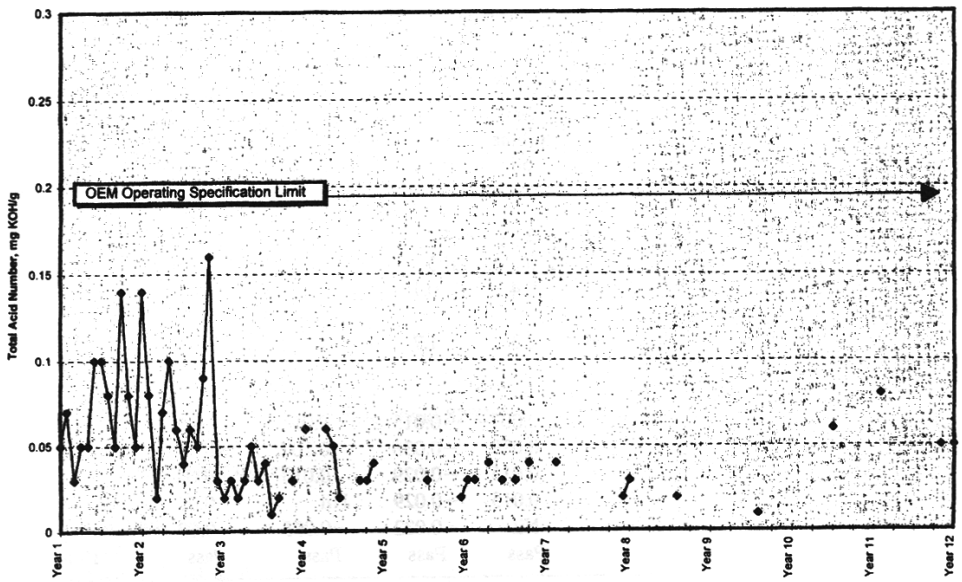

Figure 3 Thermal–hydrolytic stability of TBPP 46 phosphate ester hydraulic fluid in actual commercial use.

(Fig. 3) that degradation had not occurred. Periodic additions of makeup fluid were the only additions to the system, and a fuller's earth bypass filter system was employed. These data reinforce the effectiveness of a good maintenance program in achieving excellent operating performance from an industrial hydraulic fluid.

7. Foaming

Foaming tendency and stability can be an issue in all hydraulic systems. Commercial phosphate ester fluids pass frequently specified tests, such as ASTM D-892, which determines the maximum foam height generated under standard air introduction rates as well as the rate of collapse of the foam.

Suppliers' literature [41–43] indicates that there is little difference between the IPPP and TBPP base stocks over the ISO 22–100 grade range. All fluids generate less than 50 mL of foam, and complete collapse occurs within 20 seconds, as specified by the test method. Some suppliers may use an antifoam additive to meet this specification. Silicones are effective, but other agents have been employed as well.

D. Toxicology

Much has been written and said about the toxicology of phosphate esters over the years. Nevertheless, there is considerable concern and confusion. We shall briefly outline the state of the situation as accurately as it is currently known, but the user or potential user of phosphate esters should thoroughly investigate and evaluate the most recent data available, to reach correct conclusions about the proper degree of concern to be held and the appropriate care required in handling and use. Products made today are far safer than those manufactured in the early years when most problems occurred.

The use of recent data needs to be emphasized, since much of the early information about

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triaryl phosphates in particular was developed well before toxicological expertise and testing techniques reached today's level of sophistication. Often the precise compound or compounds involved in reported episodes or in laboratory tests were unknown, poorly defined, or misnamed. As will be seen below, one specific isomer has been identified as the most toxic of the triaryl phosphates, and its elimination results in orders of magnitude differences in the toxic responses observed. Assurance of, and confidence in, the definition of the compounds being evaluated is thus a critical factor in determining the toxicity of the product, and the appropriateness of using it in an industrial application.

It has been known since the early 1900s that exposure to organophosphate compounds can cause toxic effects in animals and humans. This phenomenon has been noted in a variety of compounds including phosphates, phosphites, phosphonates, and others. The effects can be noted visually in a deterioration of motor skills, which develops long after the exposure. Because of this, the effect has generally become known as organo-phosphate-induced delayed neurotoxicity (OPIDN). Neither carcinogenicity nor mutagenicity is involved in the observed effects.

Johnson [67,68] and Abou-Donia and Lapadulla [69] have reported and reviewed the history, symptoms, and mechanics of OPIDN. The major visible consequence of the delayed neurotoxicity is motor dysfunction, predominantly in the limbs. Triorthocresyl phosphate (TOCP) has been defined as the one of the more potent OPIDN neurotoxins in humans. The attack generally begins with the inhibition of enzyme activity in the nervous system, leading to eventual damage to the system and impairment of neural transmissions. The degree of recovery, according to these authors, can often be related to the severity of the exposure. Mild exposures do not appear to result in permanent damage.

As evidence of OPIDN and the role of TOCP became better defined, the industry took extensive steps to reduce or eliminate this isomer from commercial products. For example, tricresyl phosphate is available today with little ($<1\%$) total ortho isomer content and virtually zero TOCP.

The IPPP and TBPP esters, widely used as fluid base stocks, exhibit far less OPIDN than the TCP and TXP available through the 1960s. The trialkyl and alkyl aryl esters commercially used today also show little to no neurotoxic effects [70–73], Any effects seen are often at extremely high "limit" doses.

The synthetic triaryl phosphates are practically nontoxic by oral, dermal, and inhalation routes of exposure. Moreover, they are neither irritating to the skin or eyes nor mutagenic [74]. Several trialkyl esters, specifically TBP, TiBP, and TOP, however, are classed as skin irritants. Detailed data are readily available from the Material Safety Data Sheets published by all the various producers and other sources.

Both aryl and alkyl esters are either readily or inherently biodegradable. Speed and extent of biodegradation are related partly to the susceptibility to hydrolysis of the individual compounds. The intermediates formed during biodegradation appear to be quite nontoxic to aquatic species.

Some trialkyls (e.g., TBP, TOP), and the lower viscosity fluid base stocks (TCP, IPPP/22, TBPP/22, etc.), require certain European Union hazard labels. In the latter synthetic products this regulatory attention appears to be due to the high levels of TPP, on which anomalous, and perhaps erroneous, aquatic toxicity results have been reported. Products such as TXP and the higher viscosity IPPP and TBPP fluids do not require such labels.

The European water hazard classification scheme uses acute toxicity and ecotoxicity data in an attempt to classify products for their pollution potential. This system, commonly known as the WGK value, groups products from 0 (no pollution potential) to 3 (severe pollution potential). Phosphate esters are graded WGK 1 in this system, comparing favorably with mineral oils, which are usually rated WGK 1 or 2 [55].

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None of the triaryl phosphates that find significant use as base stocks are listed under the regulations of the International Agency for Research on Cancer (IARC), the U.S. Occupational Health and Safety Administration (OSHA), the American Conference of Governmental Industrial Hygienists (ACGIH), or the 1989 U.S. Superfund Amendment and Reauthorization Act Title III (SARA). TBP is not listed by IARC, OSHA, or SARA but does have a threshold limit value (TLV) of 2.5 mg/m^3 under ACGIH standards.

With normal and proper handling procedures and good industrial hygiene, phosphate esters can be safely used in industrial applications without undue concern for the well-being of workers and users, or the environment.

E. Maintenance of Systems

Some of the performance data discussed above indicate that proper maintenance and control of the mechanical systems can assure excellent performance and result in exceptionally long fluid or lubricant life. The system maintenance program should involve three broad areas:

1. Design and preparation of the equipment and its components.
2. Maintenance programs to preserve the mechanical integrity of the system and prevent contamination of the fluid.
3. Operating procedures that include fluid conditioning and periodic chemical analysis of the fluid.

Design and preparation of the equipment is an important first step. Since phosphate esters are excellent solvents for many organic compounds, supplier recommendations regarding seals, hoses, filters, paints, and other accessory equipment should be followed carefully. Generally [30,33], seals and hoses should be made of a fluoroelastomer or ethylene/propylene rubber. Epoxy coatings can be used, but painting of internal surfaces is not recommended. Most common metals can be used to fabricate parts and operating components. Suppliers of the phosphate ester fluids and lubricants have detailed recommendations on materials of construction; these suppliers should be consulted early in the design stage of new equipment or when conversion of older equipment to phosphates is being planned.

A number of reports have been prepared describing practical operating experience with phosphate ester fluids and lubricants [75–80]. A report by the Electric Power Research Institute [81] presents an excellent review of worldwide operating experience with phosphates esters, including problems and successes, as well as procedures and control limits recommended for phosphate ester systems. *The Handbook of Hydraulic Fluid Technology* [32] contains a thorough review of currently recommended operating and maintenance procedures for systems using phosphate ester lubricants and fluids.

Hydrolysis presents the greatest risk to fluid stability, so maintenance of low water levels is important. Further, since hydrolysis forms acidic compounds, which can catalyze further hydrolysis, acid number can be used as an excellent control parameter to both determine the condition of the fluid and maintain its stability.

Maintenance of low water and acid levels is an operation known as fluid conditioning. This can be most readily accomplished by the use of bypass filters composed of fuller's earth, activated alumina, or ion exchange resin media [82,83]. Properly designed and maintained, filtration conditioning systems will maintain moisture levels in the fluid below the recommended 0.1% by weight and the acid number below 0.2–0.3 mg KOH/g, with only periodic change of filter medium. The latest of these systems using ion exchange resins have also regenerated deteriorated fluid to satisfactory condition without removal of the fluid from the system [84,85]. Some of

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these conditioning systems are considered to be proprietary, and the fluid suppliers constitute the best source of specific recommendations on products, procedures, and analytical methods.

IV. MANUFACTURE, MARKETING, AND ECONOMICS

A. Manufacturers

Over 85,000 metric tons per year (MTPY) of phosphate esters are produced worldwide (Table 23). Of this total, the triaryl and alkyl aryl esters represent 70,000–75,000 MTPY, with each of the major trialkyls (TBP, TBEP, and TOP) representing 3000–5000 MTPY. The largest use (Table 24), consuming 55,000–60,000 MTPY, is as a flame-retardant plasticizer for a variety of plastic resins including cellulosics, polyvinyl chloride, polyurethane, and polyphenylene oxide engineering resins.

Lubricants and hydraulic fluids consume most of the remainder, 20,000–25,000 MTPY, mostly as a base stock for industrial and aircraft hydraulic fluids. Other base stock uses include specialty gas and steam turbine lubricants, and compressor lubricants. Tricresyl phosphate, and the isopropylphenyl and *t*-butylphenyl phosphates also find wide use as antiwear additives in petroleum and synthetic base stock hydraulic fluids, tractor fluids, and aircraft turbine and piston engine lubricants. Virtually all the TCP used in the lubricants industry, 1500–2000 MTPY, is used as an additive. Smaller volumes of phosphate esters are consumed in other industrial processes as antifoam agents (TBP), solvents in chemical manufacturing (TOP) and processing of uranium and other rare earth metal (TBP) [29], and as a leveling agent in floor finishes (TBEP).

The United States and Europe represent the major geographic consuming areas. Several

Table 23 Estimated 1997 Worldwide Consumption (thousands of metric tons) of Phosphate Esters

Region	Triaryls	Trialkyls	Total
North and South America	32–34	3–5	34–37
Europe and Africa	24–27	2–4	27–30
Asia	13–17	1–2	14–17
Total estimate	71–74	8–10	79–83

Source: Author's estimates.

Table 24 Estimated 1997 World Markets for Phosphate Esters (thousands of metric tons/year)

Use	Triaryls	Trialkyls	Total
Plasticizer	50–54	2–3	52–55
Lubricants/fluids	16–19	2–3	18–20
Lubricant additives	2–4	—	2–4
Other	2–4	3–5	6–8
Total estimate	71–74	8–10	79–83

Source: Author's estimates.

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Table 25 Major World Producers of Phosphate Esters and Their Production Capacity (thousands of metric tons/year)

Producer	Location		Production capacity[a]	Products[b]
FMC Corp.	Trafford Park	U.K.	30–40	1
	Nitro, WV	U.S.A.	25–30	1,2
Akzo-Nobel	Gallipolis Ferry, WV	U.S.A.	20–25	1,2,3
	Kasima-gun, Ibaraki	Japan	5–10	1
	Bitterfeld	Germany	8–12	1
Bayer AG	Leverkusen	Germany	10–12	1,2,3
Daihachi Chemical Industry Co.	Handa, Aichi and Higashi, Osaka	Japan Japan	5–10	1,2
Ajinomoto Co., Inc.	Yokkaichi, Mie	Japan	5–10	1
Monsanto Company	Bridgeport, NJ	U.S.A.	4–5	3
	Newport	U.K.	3–4	3
Protex, SA	Chateau Renault	France	<1	2
Croda Chemicals, Ltd.	Goole	U.K.	<1	2
BASF	Ludwigschafen	Germany	<2	2
Hodogaya Chemical Co.	Koryama, Fukushima	Japan	<1	1
Mitsubishi Gas Chemical Co.	Tokyo	Japan	<2	1
Showa Ether Co.	Aiko-gun, Kanagawa	Japan	<1	1

[a] Author's estimate.
[b] 1, Triaryl phosphates; 2, trialkyls; 3, alkyl aryl phosphates.

producers exist in each of the major market areas (Table 25). Estimated world capacity totals over 125,000 MTPY. Since most companies produce a variety of products at the same plant location and sometimes in common equipment, capacity figures are difficult to define, but it is estimated that capacity for the triaryl and aryl alkyl esters approaches 110,000 MTPY or more.

B. Suppliers

Phosphate esters are sold commercially by basic chemical producers and fluid compounders under a variety of trade names to both the fluid/lubricant and lubricant additive markets. Table 25 lists the major suppliers and their manufacturing locations. A list of commercial product names appears in Table 26, which includes fluids that are pure phosphate ester base stocks, as well as those in which the phosphate is blended with either petroleum or other synthetic base stock.

Except for the aircraft fluids in which TBP and/or an alkyl diaryl ester is the major component, almost all the important fluids and lubricants are based on the synthetic IPPP and TBPP triaryl phosphates.

C. Economics

Phosphate ester industrial fluids are more expensive to produce than petroleum and some of the other more common synthetic base stocks. Costs depend largely on petrochemical raw materials, such as butylene and phenol, and the relatively complex processing and purification procedures. Industrial fluids, such as those commonly used in primary metal refining and fabricating mills,

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Table 26 Suppliers of Phosphate Ester Hydraulic Fluids and Lubricants

Company	Trade name[a]	Types of product
Ajinomoto Co., Inc.	Reolube HYD	Fluids
Akzo Nobel	Fyrquel	Fluids, lubricants
	Syn-O-Ad	Additives
	Fyrtek	Fluids
Albright & Wilson, Inc.	Duraphos	Additives
Bayer AG	Disflammol	Additives
BP Oil	Enersyn SFD	Fluids
Castrol Inc.	Anvol PE	Fluids
Daihachi Chemical Industry Co.	—	Fluids, additives
D.A. Stuart Co.	Dasco	Fluids
Exxon Corp.	HyJet	Aircraft fluid
	Imol	Fluids
FMC Corp.	Durad	Additives
	Reolube HYD	Fluids
	Reolube Turbo Fluid	Lubricants
Fuchs Mineraloelwerke GmbH	Phostex	Fluids
Houghton International, Inc.	Houghto-Safe	Fluids
Metal Working Lubricants Co.	Metsafe	Fluids
Mobil Oil Corp.	Pyrogard	Fluids
	Pyrotech	Fluids
Monsanto Co.	Skydrol	Aircraft fluid
Pennzoil Corp.	Pennsafe	Fluids
Pacer Lubricants, Inc.	Pyro-Safe PE	Fluids
Shell Oil Corp.	Hydraulic Fluid SFR	Fluids

[a] Names listed are trademarks or trade names of the respective companies. A number or letter designation often follows the trade name to further define the product. Some suppliers use the same trade name for fluids made from base stocks other than phosphate esters.
Source: Ref. 56 and private communications.

generally sell for three to five times the price of petroleum oils: that is, in the (U.S.) $10–$15/gallon range. Other specialized fluids and lubricants have prices up to $20/gallon; the highly refined products such as the aircraft and electrohydraulic control fluids can reach over $30/gallon in small quantities.

At these market prices, phosphate ester fluids are among the higher priced of the more common synthetic fluids such as organic acid esters and poly(α-olefins). They are not as expensive as others, such as silicone and fluorocarbon fluids.

The higher price for phosphate ester fluids is justified on performance characteristics, especially lubricating ability, resistance to burning, and proven longevity in use.

Phosphate esters provide the highest level of fire resistance and safety when all the moderately priced anhydrous fluids rated as less hazardous are considered. Their high fire points and high flash points enhance their resistance to ignition, and their low heat of combustion makes them the only self-extinguishing fluids in their price class. Therefore, when personal safety factors and equipment preservation are of paramount importance, phosphate esters may be the most cost-effective fluid base stocks yet developed.

Cost effectiveness is also determined by the longevity of the fluid or the frequency of replacement. Phosphate esters can be readily maintained and/or regenerated by in-line conditioning systems. Thus, a user can comply with environmental issues dictating the need to reduce

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leakage from systems and to minimize disposal quantities. Proper care and maintenance of the system and fluid minimizes top-up costs and virtually eliminates disposal costs, while allowing operation for many thousands of hours (>100,000 h in some instances) between fluid changes.

V. OUTLOOK

Phosphate esters were among the earliest synthetic base stocks developed and are relatively mature products in many of their market segments. Engineering design improvements in materials of construction and operating pressures have enabled the use of lower cost materials in many market segments pioneered by phosphate esters. In other uses, such as in the aircraft and power generation (electrohydraulic control) markets, where safety is critical and high operating pressures and temperatures are common, phosphates have continued to grow and find wider use.

Being excellent lubricants as well as fire resistant, phosphate esters have always held promise in other industrial uses. Extensive laboratory and field development effort has been directed at the use of phosphates as turbine main bearing lubricants [78,81,86] and is the result of many years of effective performance in stationary gas turbines, mainly in gas pipeline pumps. Continued occurrence of fires in this area has, however, renewed interest in applying phosphate ester lubricants to aeroderivative turbines (which use polyol ester aircraft turbine lubricants) for pipeline and other uses [86]. Also, recent developments in Russia [77] have resulted in the decision there to design main bearing systems that will use lubricants based on trixylenyl phosphate for all new large (>1000 MW) and small steam turbines.

Perhaps the most promising and most interesting use that may develop over the next several decades is the use of phosphate esters as vapor-delivered lubricants for low heat rejection (adiabatic) engines. This work, pioneered by E. E. Klaus, E. E. Graham, J. L. Duda, and others at Pennsylvania State University and supported by the U.S. Department of Energy and other agencies [87–89], continues to be the subject of active research efforts [90–95].

Low heat rejection engines, while expected to achieve high fuel efficiencies with reduced emissions, will place exceptional strain on the thermal stability of the lubricants both in the combustion chamber and in the lubricant sump. Vapor delivery of the lubricant avoids the latter problem, since the bulk of the lubricant can be kept at moderate temperatures until it is delivered to high temperature frictional contact zones (piston ring or turbine bearing). Work to date has shown that triaryl and/or trialkyl phosphate vapors can be delivered directly to the walls of the combustion chamber in very low concentration which, while providing adequate lubrication, will not result in excessive engine exhaust emissions or harmful deposit formation. The concept has been demonstrated on a laboratory diesel engine [93] and on a jet turbine engine at Wright Patterson Air Force Base. Next-generation engine development work is planned by both the U.S. Air Force and several commercial engine manufacturers [96]. The significant body of work published in this area was recently reviewed by Rao [97].

Phosphate esters may also play an important role as a co-base stock with other synthetics in the lubrication of low-heat-rejection diesel engines being developed as intermediates or alternates to the truly adiabatic engine [90]. This work has been sponsored in part by the U.S. Department of Energy and several industrial companies.

When used as quench oils in metal-forming operations, phosphate esters [98,99] can provide health, safety, and performance advantages. Compared to mineral oils, phosphates offer better oxidative stability and longer bath life; lower volatility and lower VI reduce evaporation, misting, and drag-out; superior ignition and fire resistance reduce spattering, fire hazards, and smoke generation. In addition, the phosphate quench oil applies a wear- and corrosion-resistant coating to ferrous surfaces.

Another new application involves replacement of graphite as a forging lubricant [100]. The

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phosphate emulsion formulation deposits a good lubricating film on the press and avoids dirty and hazardous mists and soot generated by the graphite system.

In summary, environmental issues have become a driving force that is generating renewed interest in phosphate esters for a variety of applications. Extraordinarily low volatility and high stability allow phosphates to be delivered in appropriate quantities in environmentally friendly vapor phase lubrication systems. Stability and capacity to be regenerated are advantages that result in reductions in the quantities released to the environment or being sent to landfill or waste treatment. Ironically, some of the weaknesses noted in the past about phosphates are becoming advantages in the environmental sphere. As more is learned of toxicology, phosphates appear to be holding their own in comparison with other common lubricants and fluids. Esters, such as the trialkyls, which have been dismissed for poor hydrolytic stability, may have advantages in rapid biodegradability and less persistence in the environment.

The changing environment has led to, and shows continuing promise toward, a remarkable renewal of research and development into these products, which have been commercially available for so many decades.

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